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Water – A magic solvent for biomass conversion

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ABSTRACT

Hydrothermal biomass conversion processes provide the opportunity to use feedstocks with high water content for the formation of energy carriers or platform chemicals. The water plays an active role in the processes as solvent, reactant and catalyst or catalyst precursor. In this paper, the different hydrothermal processes of carbonization, gasification and liquefaction are introduced and the specific role of water is discussed for each of them. The high reactivity of the polar components of biomass in hot compressed water and its changing properties with temperature are the key to obtain high selectivities of the desired products. Despite the obvious advantages of hydrothermal conversion examples for industrial applications are rare. The main reason for not commercial application of water in the high temperature state is that there are no products that can be sold with profit and cannot be produced cheaper, with less capital risk, and with more simple processes.

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1. Introduction

Hydrothermal biomass conversion processes are interesting techniques to produce renewable solid, liquid/tarry or gaseous fuels. The most important advantage of hydrothermal processing is that wet biomass, typically with 70 wt.% or more water can be converted without drying. Drying of biomass to optimal water contents below 10 wt.%, as necessary for "dry" biomass conversion processes, costs substantial amounts of energy [1]. Therefore, hydrothermal conversions are attractive to extent the resource base for bioenergy production. The reason why no drying is necessary is that hydrothermal processes are conducted in liquid water. The water inside the biomass is the same component as the solvent. In addition the reaction is supported by water as catalyst or catalyst precursor as well as reactant. Every particular role of water is connected with the special properties of superheated liquid water above 100 °C [2–6]. The reaction temperatures are above 100 °C; therefore, hydrothermal processes require a pressure above the vapor pressure of water at the corresponding temperature to keep water in its liquid phase. This means that hydrothermal processes are chemical reactions in a solvent; in this case a solvent changing its properties depending strongly on temperature. As a consequence the chemical processes are influenced by the different solvent properties depending on reaction conditions. By adjusting the reaction parameters the reactions can be tuned selectively to obtain different products, namely solids (biochar), liquids, or gases (methane and hydrogen).

2. Overview of hydrothermal conversion processes

The hydrothermal processes can be assigned in terms of reaction temperature and, accordingly, pressure (see Fig. 1). At relatively low temperatures pretreatment methods are conducted. The most important one is "steam explosion" [8,9]. Here, the biomass is heated up under pressure typically to 140–240 °C. Then, the pressure is reduced rapidly to ambient pressure e.g. by opening a valve. The water inside the biomass evaporates thereby disrupting its structure like in an explosion. This way the cellulose and the lignin, covering it, are separated. This is important because in non-treated biomass this lignin protects the cellulose fibers against attack of enzymes, solvents or other agents. Therefore, steam explosion is a useful pretreatment method e.g. for bio-ethanol production from lignocelluloses by fermentation. By this pre-treatment, the yield is increased because of the higher reactivity of cellulose [8,9]. This

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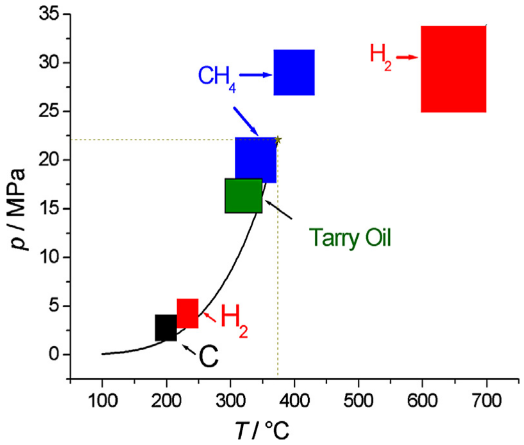

Fig. 1. Overview of different hydrothermal biomass conversion processes and the vapor pressure curve of water (simplified) [7].

points to an important aspect of hydrothermal processes: They can be combined with biological or biochemical processes because they are carried out in the same solvent [10]. Depending on the reaction conditions and especially in the case if acids are added the biomass is not only disrupted, but already partly hydrolyzed during steam explosion [11].

Hydrothermal carbonization (HTC) occurs at around 200 °C. Here, the carbohydrates are completely solved after hydrolysis and polymerize subsequently to a product called "HTC-coal". The process usually needs 2–4 h reaction time and has been demonstrated with a lot of different types of biomass [12–17]. This "HTC coal" has a heating value similar to lignite, but with a higher content of volatile substances and a higher biodegradability in soil, which is important if it is used for soil improvement [18]. Here, the phytotoxicity of fresh HTC coal is an important issue to be considered, likely a consequence of water soluble products like phenols, which are adsorbed at the HTC coal surface [19]. The production of HTC coal overcomes three major disadvantages of untreated biomass as fuel:

A) The heating value of untreated biomass is low because of the high oxygen and water content. By the elimination of water (and smaller amounts of CO_2 [20]) the HTC coal has a higher heating value and lower oxygen content than biomass [14,16,17,21,22].
B) Mechanical dewatering of HTC products is very effective because of its highly hydrophobic properties. Studies with sewage sludge show, that the easier dewatering alone justifies hydrothermal carbonization as a first drying step. Thermal drying, usually applied as the second step, needs much more energy in the case of biomass, where mechanical dewatering leaves a lot of water in the material. On the other hand the water has to be removed to burn the biomass and to reduce transportation costs [12,23].
C) Biomass has a high potassium content. This leads to low ash melting temperatures, which makes burning more complicate. Special techniques are required to prevent corrosion and to handle the ash melt or the burning temperature is limited to below 600 °C. This is too low for efficient power generation, like in conventional power plants like pulverized coal firing systems with 1300–1500 °C. During hydrothermal carbonization the potassium is solved in the water. The lower potassium content in the ash leads to higher ash melting temperature of e.g. 1200 °C. This is similar to the ash melting temperatures of fossil lignite [13,24].

In regard of the aspects mentioned above, HTC coal is a more suitable energy carrier than untreated biomass. In addition, HTC coal can be modified to be used as adsorbent for organic compounds or as an ion exchanger [25,26]. In the case that not biomass [27,28], but pure compounds like glucose are used in the process, advanced materials like micro- or nano-spheres as well as nano-tubes can be produced [29]. At slightly higher temperature aqueous phase reforming (APR) can be performed by means of catalysts to produce hydrogen or hydrocarbons [27,28]. This process for hydrogen production is only possible at very low concentrations of the feed material because of thermodynamic limitation [30]. At higher concentrations methane is the thermodynamically favored product. For this APR process catalyst like Ni, Pt, Pd and others are used [28]. Since these are solid catalysts, they cannot work with solid biomass. In most cases hydrogen-rich, soluble compounds produced from biomass show the highest hydrogen yields. This process is therefore appears to be useful for aqueous effluents of other hydrothermal processes [31] or other aqueous effluents [32]. Poisoning and long term stability of the catalyst is often a challenge of this process [33]. The hydrogen produced can be used for hydrogenation of the feedstock to produce hydrocarbons [28] or to up-grade bio-oils [34]. For this process, in principle the same type of catalyst can be used as for hydrogen production before, but the selectivity varies [27,28]. After formation of hydrogenated products, other reactions like the formation of aromatic rings can be carried out [35]. Therefore, APR is discussed as process to produce a substitute for terephthalic acid.

In the temperature range between 300 °C and 350 °C hydrothermal liquefaction takes place [36–39]. The process is also known under the original SHELL trademark HTU$^{(r)}$ for "Hydrothermal upgrading" [40]. Here, the biomass is converted to a highly viscous tarry oil of a high heating value [1]. Some significant differences occur compared to the dry conversion technology, the flash pyrolysis. In hydrothermal liquefaction and at optimized conditions no solid product is formed. In flash pyrolysis the solid yield is usually in the range of 20 wt.%. Very short reaction times of a few seconds at 500–600 °C are necessary to reach high yields of pyrolysis oil of around 60 wt.%. This oil is an intermediate and longer reaction time would convert it to gas and solid. As a consequence very fast heating-up (ca. 1000 K/s) and rapid cooling down of the vapors formed during pyrolysis have to be realized. For hydrothermal liquefaction this is not necessary. No further reactions to solid or gaseous products occur at reaction conditions, with much lower temperature. The heating value of the hydrothermal liquefaction product (30–36 MJ/kg) is much higher than that of pyrolysis oil (20–25 MJ/kg). The reason is that pyrolysis oil includes a wide range of polar compounds like acids, alcohols, aldehydes and even sugars. In addition, ca. 15–20 wt.% of water is formed during pyrolysis that is in the pyrolysis oil after cooling down. In hydrothermal liquefaction polar, oxygen-containing compounds are solved in the water and only the compounds of lower oxygen content, namely phenols are found in the oil phase [1].

A special issue of liquefaction is the decomposition of lignin [41]. Here the goal is to get phenols, e.g. for the production of resins. Lignin is less reactive as lignocellulosic biomass and requires therefore a temperature of around 400 °C and maybe the support of a catalyst.

Near the critical point of water there is the range of catalyzed gasification to produce methane. For this reaction noble metal catalysts are necessary [42–44]. The active metals are Ni, Rh, Pd, Pt, suitable for hydrogenation of e.g. CO to methane [43]. There are two approaches applying subcritical or supercritical[1] conditions. The subcritical approach has the advantage that salts are mostly solved and therefore plugging by salt precipitation is less likely [45]. The supercritical reactions have the advantage that organic

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[1] The term "sub- or supercritical" here refers, as usually done, to the critical point of water as the solvent. This does not mean that the mixture is supercritical in the sense that pressure and temperature are above the critical point of the mixture.

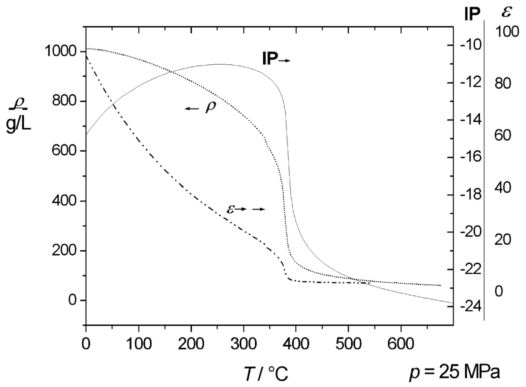

Fig. 2. Properties (density, ionic product and relative static dielectric constant) of water as function of temperature at 25 MPa ([55,56] data from [57]).

compounds are better solved [46]. In both cases poisoning of catalysts by salts is observed [43]. Detailed investigations of the salt water systems show very interesting properties and different opportunities to handle the salt deposition [46,47]. A very important aspect here is that some salts form solid and some, mainly potassium salts, form a liquid phase of higher density compared to the supercritical water phase [47,48]. The possibilities to separate salts are precipitation [46], solvation in salt brines [47] and the use of a hydro-cyclone [49] (Fig. 2).

In the range of 600–700 °C the so-called supercritical water gasification (SCWG) is conducted [7,30,44]. Here the goal is to produce hydrogen, which is the reason for the high temperature. On the other hand this high temperature makes the choice of reactor material challenging [30]. In an ideal case, the conversion to hydrogen and CO_2 as major and methane as minor compound is complete. Only the inorganic compounds should be left in the aqueous effluent. Experimental studies show, on the other hand, some hurdles: proteins limit the reaction rates [50,51] and higher dry mass contents inhibit complete conversion [30]. Acetic acids and phenols usually are found in the effluent aqueous phase, if the conversion is not complete. To reach complete conversion, especially at higher conversion and if possible, lower temperature different catalyst including activated carbon are tested [52,53]. The CO content of the product gas formed in biomass gasification is usually below 1 vol.%. Model compound gasification usually leads to higher CO contents, because the potassium salts in the biomass catalyze the water-gas shift reaction (see below) [7,30]. Then, the product gas can be used as synthesis gas to produce e.g. methanol [54].

3. Properties of water

Water at ambient conditions is a polar solvent of polar molecules. It is a good solvent for polar compounds and salts. On the other hand it is a weak solvent for non-polar compounds and gases like hydrogen or nitrogen [58]. If water is heated up, the density decreases. In consequence and because of the increased thermal movement of the water molecules, the interference of different water molecules is weaker. This leads to fewer and less stable hydrogen bonds, although clusters by hydrogen bonds still exist at high temperature [59–61]. The second consequence of the lower density is that the relative static dielectric constant decreases [62]. Therefore, with increasing temperature the solvent polarity decreases. At supercritical conditions at e.g. 550 °C and 20 MPa, water behaves as a nonpolar organic solvent like pentane with good solubility for organic components and gases and low solubility for salts [63,64]. But the single water molecules are still polar. In the case that a polar compound or ion is present in the water, the water molecules in its nearer environment are attracted. In the case of higher multi-valent cations the strong interaction to the oxygen atom leads to an elimination of H^+ and a strong acidic behavior. Calculations for bi-valent cations (here Ca^{2+} and Sr^{2+}, at water densities between 0.29 and 0.087 g cm^{-3}; [65]) lead to a density, which is increased by a factor of 30–100 compared to bulk density. In the case of mono-valent anions the hydrogen atom comes closer to the ion than the oxygen of the water molecule in the solvent shell to a cation. This leads to the observation that salts, which are usually neutral like NaCl become basic by formation of HCl [66]. This influences chemical reactions. As a rule of thumb, weak acids like dissolved CO_2 become stronger [67,68] and strong acids like HCl become weaker [69]. From the thermodynamic perspective the reason is that the dissociation of weak acids is usually endothermic [67]. As water shows self-dissociation also the formation of H^+ and OH^- is influenced by the strong clustering effect [70]. This leads to a high “local concentration” of H^+ and OH^- ions accelerating e.g. the Beckmann and Pincol-Pinacolone rearrangement, monoterpene alcohol synthesis as well as the Cannizzaro and Heck reaction, especially slightly above or very close to the critical point of water [71–78]. Here the H^+ and OH^- ions can move very fast inside one cluster leading to a high reactivity slightly above the critical temperature, although the total concentration is lower than in sub-critical water [79]. (For a discussion of micro structuring effect on chemical reactions see [56]).

Also, water is a weak acid and base, becoming stronger because the dissociation is endothermic. Therefore, the ionic product is higher at subcritical conditions than at ambient ones [62]. On the other hand the low density of water above its critical point leads to break-down of the solvent shell and the ionic product decreases drastically at low densities [80]. Looking at chemical reactions the reaction rates of acid-catalyzed reactions are higher than assumed by the ionic product. The reason might be that water fulfills the function of the H^+ ion or micro-structuring effects [3]. In both cases simply a hydrogen atom of water comes very near to a reactive center of an organic molecule inducing a reaction, which at normal conditions is caused by acids.

Another important aspect is the role of the dielectric constant [81]. It influences solubility and also chemical reactions. In the case an intermediate state of a chemical species during a certain reaction has a higher polarity than the educts or products a polar solvent decreases the activation energy and increases the reaction rate. Concerning water at increased temperature and pressure the question occurs, if the macroscopic dielectric constant or a local dielectic constant created by the solvent effects is determining [82,83]. Solvent shells around organic compounds influence organic reactions in supercritical water. Concerning the influence on chemical reactions it is experimentally very difficult to distinguish which property of water is relevant, because they all change with density and temperatures [56]. For a more detailed discussion of the role of water see [2–6].

For the chemistry of biomass conversion it can be concluded that water is very reactive at every condition but the properties as solvent change. This influences solubility and the stability of ions.

4. Driving forces: thermodynamic and kinetics

In Fig. 3 the gas composition as function of temperature is shown in case of thermodynamic equilibrium assuming a mixture of glucose and phenol as a substitute for biomass. An important result is that thermodynamics predict a nearly complete gasification at any temperature. The second important finding is that methane is the preferred product at low and hydrogen the preferred product at high temperatures at the given concentration like 10% (g/g) (model compound or dry matter content) [84–86]. At low temperatures an increased hydrogen formation is possible also at low

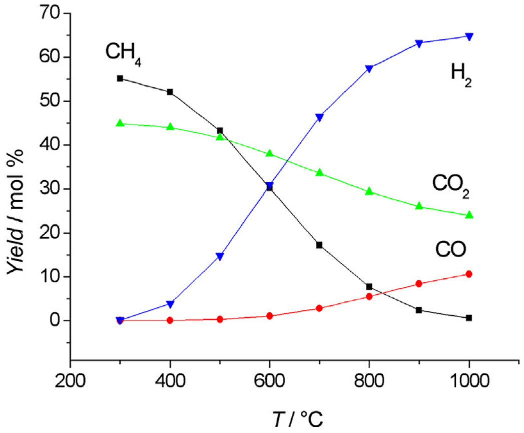

Fig. 3. Calculated gas yields for a glucose/phenol–mixture representing biomass as function of temperature at 30 MPa with 10 wt.% dry matter content (5.4 wt.% glucose und 4.6 wt.% phenol, 25 MPa calculated with Aspen Plus, Rgibbs reactor, "PENG-ROB" method) Feedstock content in equilibrium: Glucose <10–20 mol%, Phenol 10–18 to <10–20 mol% deceasing with temperature.

concentrations. This can be explained by applying the principles of Le Chatelier to the reactions of hydrogen (1) and methane (2) formation.

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2 \tag{1}$$

$$C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2 \tag{2}$$

In this generalized equations, the formation of hydrogen requires water unlike that of methane. Consequently, the presence of a large excess of water prefers the formation of hydrogen. The methane formation is slightly exothermic and therefore occurs at lower temperature. High hydrogen yields at low temperatures are only possible at very low concentration and, correspondingly, high water excess. This is the basic idea of aqueous phase reforming. At every temperature in Fig. 3, the CO yield is low. The reason is the influence of a water excess on the water-gas shift reaction (3).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3}$$

The reaction to form CO is slightly endothermic and should be preferred at higher temperatures. This is also visible in Fig. 3. On the other hand the large excess of water counteracts this trend by shifting the equilibrium (3) to the right hand side reducing the CO yield. Here, we see the first important role of water in hydrothermal biomass conversion: It is reactant in the water-gas shift reaction (3) and necessary for high hydrogen yields.

The gas composition as predicted by thermodynamics is not always attained. Then, the use of catalysts becomes necessary. As an example, hydrogenation catalysts can be used for hydrogen formation during aqueous phase reforming at low temperatures (see above). As catalyst always catalyzes the chemicals pathways in the direction to equilibrium, the same selection of hydrogenation catalyst are used for the formation of methane at near critical gasification (see above). Methane formation by CO hydrogenation is kinetically inhibited and the experimental yields of methane are low without catalyst except from acetic acid, which is a precursor for methane formation by decarboxylation. The water-gas shift reaction (3) is also kinetically inhibited. Here, alkali salts are active as catalysts, which usually are part of the biomass [87]. At supercritical water gasification the temperature is so high that no other catalysts, e.g. noble metals, are necessary for gas formation from biomass. In spite of this, to overcome the hurdle of decreasing gas yield with increasing dry mass content, different catalyst are applied [88,89]. These are hydrogenation catalysts, as mentioned above, and carbon. Carbon has the advantage of high resistance to the strange conditions of temperature and pressure and was successfully applied [52,53].

The reactions of biomass and biomass degradation products occurring in liquid water are catalyzed by acids, bases, or water. This is important for hydrothermal carbonization and liquefaction. The increased ionic product of water leads to a catalysis of both, reactions requiring OH^-_{aq} for a higher reaction rates and those needing H^+_{aq}. The strong connection to the role of water will be discussed in the next chapter. To increase selectivity toward one type of these reactions, acids or bases are added to accelerate of the desired reaction path. Often acids are used to improve reaction rates of hydrothermal carbonization and basic salts to accelerate liquefaction [14].

5. The role of water in the different processes

A characteristic feature of hydrothermal reactions is the high hydrolysis rate of biomass. As a consequence, biomass is partly or completely solved in water. The solved intermediates show consecutive reactions [90]. It has to be pointed out, that these degradation reactions might be influenced by solvent–solute interactions, which has been investigated for the aldol addition [91]. The fast degradation in the water solvent avoids heat and mass limitations as occurring in dry processes where a solid biomass particle is reacting in a gaseous environment. This is especially the case, if wet biomass with typically low lignin contents is converted. Here, the water inside the biomass structures promotes heat transfer and chemical reactions. The fast transfer of the reactions into the liquid phase is the reason for the lower temperatures necessary for hydrothermal conversions compared to the corresponding dry ones.

The chemistry of hydrothermal carbonization is complex and still not fully understood [12,14,16]. On the other hand it is common sense that carbohydrates and partly lignin hydrolyze to intermediates [90,92]. These intermediates show further reactions e.g. to furfural and hydroxymethylfurfural (HMF) [90,93]. This is an acid catalyzed reaction under elimination of water. Acids are formed as by-products; therefore the reaction is autocatalytic. The carbonization product is mainly formed by polymerization of the intermediates, especially HMF [94,95]. Some parts of lignocelluloses, e.g. most of the lignin, remain unsolved [96]. An important finding is the high reaction order of HMF-Polymerization [97,98]. This hints to an emulsion polymerization. First, a second liquid phase is formed and then polymerization occurs. This assumption is confirmed by observation in solid inclusion as very small high-pressure view cells, showing a second liquid phase, which becomes dark afterwards. Anyway, although this is an explanation for the formation of micro sheers by hydrothermal carbonization [21] the assumption is not proven and not common sense. The solubility of HMF should be sufficiently high at the relevant subcritical conditions, but no data from solubility studies are available. As already mentioned above, the hydrolysis of lignocelluloses is not complete, because the lignin with its lower reactivity protects the carbohydrates from the attack of water. In this case reactions similar to dry conversion processes occur under elimination of small molecules of lower volatility, or in case of hydrothermal processing higher solubility, finally leaving a solid product. The hydrothermal reaction is faster than the dry conversion because of better heat-transfer and some helpful reactions with water. However, a smooth transition between dry conversion (torrefaction, [99]), conversion in steam (e.g. biomass steam processing [100,101]) and hot water is observed [102]. Here we see the importance of water as reactant in hydrolysis, catalyst/catalyst precursor in the occurring reaction and as solvent. In this case a solvent with changing properties, enable the formation of a second phase at certain conditions and at other not. In addition a solvent with high heat transfer properties avoiding temperature differences inside biomass particles.

At conditions slightly above those of HTC, we find the region of aqueous phase reforming. Here, thermodynamics allow the formation of hydrogen at low educt concentrations. So far, this has successfully been done with compounds derived from biomass not with biomass itself. The fundamental question asks for what the catalyst is doing. The challenge of applying heterogeneous catalysts is that in the beginning, there are two solids, catalyst and biomass. A direct reaction is therefore very unlikely. More reasonable is the reaction of solved molecules, produced by the degradation of biomass. In APR the temperature is high enough for complete degradation. Anyway, higher molecular weight compounds would be present in the mixture as well. This leads to a high risk of charring and as consequence, catalyst poising in the case of biomass conversion. This is the main reason why usually monomeric compounds with low molecular weights are used as educts. The catalysts used in APR are hydrogenation catalysts. They catalyze the elimination/formation of hydrogen but also its reactions. The hydrogen formed from the biomass is able to react with the biomass degradation compounds to form hydrocarbons. Concerning this consecutive reactions the various catalysts behave differently [28]. The thermodynamic concentration limitation becomes irrelevant, because the hydrogen leaves the equilibrium by this reaction. The increased solubility for hydrogen, educts and products as well as the increased diffusion rates are important advantages in doing heterogeneously catalyzed reactions in hot, compressed water [103,104].

At increased temperatures hydrothermal liquefaction occurs. At this point it makes sense to compare hydrothermal liquefaction with the corresponding “dry process” to understand the role of water [1]. To produce a liquid fuel form dry biomass, fast or flash pyrolysis is applied usually around 500 °C and at very short reaction times in the order of seconds. A complex product mix of several hundred components is formed (see above) containing up to 30 wt.% of water. The short reaction times combined with high heating and cooling rates are necessary, because pyrolysis oils are intermediate products. At longer reaction time the oil components further reacts to coke and gases [2]. The high temperatures are necessary to split-up and volatize the biomass. At lower temperature mainly char is formed by elimination of smaller, volatile compounds from the solid particle. In the hydrothermal process the reaction with water enables complete conversion of biomass by hydrolysis instead of thermolysis. Consequently, lower temperatures are necessary. At these temperatures, thermodynamics predict complete conversion to gases (see above). In fact the gas formation rate is low and there is no necessity to use short reaction times. Obviously the gas formation is kinetically inhibited. Although some studies report the formation of solids, e.g. inorganic precipitate of incomplete conversion of too large particles, other reports find no or very low solid formation [36,39,105,106]. For hydrothermal liquefaction usually compounds like KOH or K_2CO_3 are used as catalyst [107]. Basic catalysis may help to avoid coke formation; the main reason is the high solubility of different compounds in subcritical water. The presence of this potassium salts leads to a measurable reduction of HMF, which usually is able to polymerize [108] or forms humines with carbohydrates [90,109]. It is assumed that this is an indirect effect of the catalysis of the water-gas shift reaction (3), where the active hydrogen formed hydrogenates the HMF [110].

By fast pyrolysis and hydrothermal liquefaction in principle the same products are formed but in different composition [1]. This is remarkable, because the chemical mechanism seems to be an ionic one at hydrothermal conditions [2] but which cannot be ionic at dry conditions with missing stabilization by water as a solvent. As an assumption, water as solvent opens a low-temperature, ionic pathways to products, which are formed via free radical reaction in dry pyrolysis. Consecutive reactions of these products could only be free-radical ones with high activation energy. Therefore, in dry pyrolysis the intermediates show fast consecutive reaction but not at hydrothermal conditions. The main difference is that due to the excess of water and the phase separation after reaction, polar compounds like organic acids and small polar components like alcohols are found in the aqueous phase. The organic phase mainly consists of phenols. As seen in Fig. 3 the phenols are thermodynamic not stable, but obvious these compounds have no chance to react to gases at these low temperature and in water. The reaction in water with phase separation afterwards leads to an extraction of the polar compounds. By support of water elimination in the hydrothermal conversion, no sugars are found in any phase, which are typical products found in pyrolysis oil. This extraction of polar compounds after reaction simply by phase separation leads to a product of higher viscosity, lower oxygen content and higher heating value compared to pyrolysis oils. An important observation is the relatively high yield of phenols. Pure carbohydrates form also phenols [2,111], they are not only derived from lignin. The formation of phenols is explained by the departing of small compounds formed from carbohydrates, catalyzed by potassium [111]. Here, water is important as solvent for the potassium salts and the compounds forming phenols to enable the reaction. However, in regard to process development, the use or treatment of the aqueous phase formed during hydrothermal conversion has to be considered.

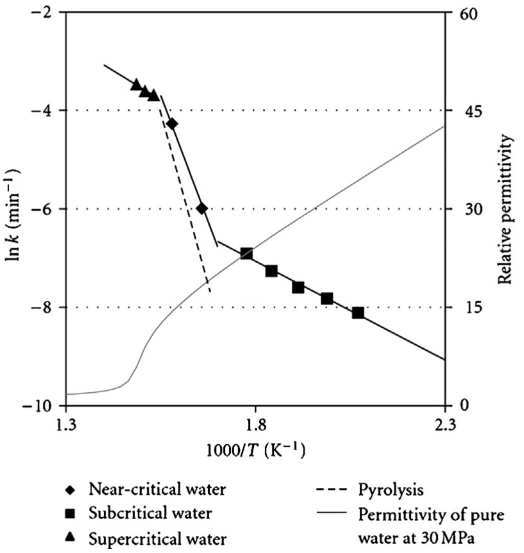

Fig. 4. Arrhenius plot of guaiacol degradation in near critical water [112] compared with experimental values from experiments in sub- and supercritical water [115] and via pyrolysis [116] (Copyright © 2012 Daniel Forchheim et al. [112]).

As mentioned above, the splitting of lignin, derived e.g. from the pulp and paper production, is usually conducted at around 400 °C. The reason for its lower reactivity is the less and, because of the complex three-dimensional structure, hardly accessible ether bonds. To understand the chemistry, studies of the degradation of model compounds like guaiacol are useful. Fig. 4 shows the Arrhenius-plot of this reaction in water at different temperatures [112]. There is a kink between the sub-critical and near-critical data indicating a change in the reaction mechanism. As the data in near- and supercritical water are very similar to the pyrolysis reaction rates, it is likely that the high-temperature pathways occur via free radicals [113]. At lower temperatures, ionic hydrolysis pathways occurs, which is not possible in dry pyrolysis. To conclude: In lignin splitting the role of supercritical water is to act as a solvent. This is important because often hydrogen with a hydrogenation catalyst is

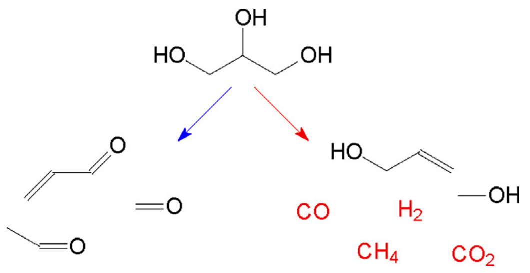

Fig. 5. Typical products of glycerol conversion in water. Left: products from low temperature/high pressure pathway, Right: products from high temperature/low pressure pathway [117].

used to support the lignin decomposition, and hydrogen solubility is very high or even complete at these conditions.

Also, reactions studied in the context of up-grading bio-oils from pyrolysis are mainly dominated by free-radical reactions due to the low number of reactive polar bonds [114].

A change in the reaction mechanism as shown in Fig. 4 has been studied before, e.g. for the reaction of glycerol in water [117]. At subcritical conditions and above the critical temperature at higher pressure and similar density, products formed via ionic intermediates are found. These are different aldehyde, ketones and others (Fig. 5). Larger amount of gases are only formed at lower densities above the critical temperatures of water (Fig. 5). These gases and other products like methanol, indicate a free radical reaction pathway [117,118]. For all products in the lower temperature range a reaction network was set-up basing on the catalysis by $OH^{-}{}_{aq}$ and $H^{+}{}_{aq}$ formed from water. This way the ionic product of water controls the importance of this network. For the high-temperature reactions free-radical reaction pathways were created [117]. So in the model, both reaction networks compete: At lower temperature and higher density the ionic reaction pathways are superior because of the high ionic product of water. At higher temperature the ionic reaction pathways are suppressed because of the low ionic product and the free-radical reaction pathway dominates. The measured kinetic rate coefficients and the calculated ones of the global reaction rate are shown in Fig. 6. Near the kink, the derivations between modeling and experimental results are larger, likely because the model is not considering any interference between the both reaction networks.

As a consequence of the free-radical nature of biomass gasification in supercritical water, free-radical scavengers reduce the reaction rate. These are Maillard products formed from protein-containing biomass [50,51] and phenolic compounds [119]. Another consequence of the free radical mechanisms are differences in the gas composition after gasification of alcohols depending of the number of carbon atoms. The dominance of β-scission cracking leads to higher methane and lower hydrogen yield, if the number of carbons of the organic acid is even [120].

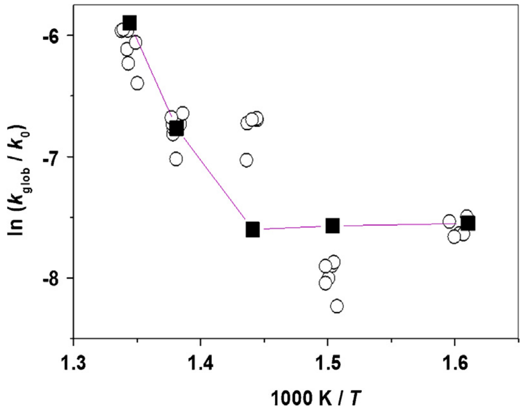

Fig. 6. Arrhenius-plot [117] of the over-all rate coefficient: Cycles are measured and rectangles are calculated data.

From an historical point of view, free radical reactions in supercritical water have been intensively studied in view of oxidation reactions. The goal was to destroy hazardous waste by supercritical water oxidation (SCWO) promising nearly complete conversion because of the absence of mass and heat transfer limitations. Even early studies of SCWO show an unexpected high reaction rate of the water-gas shift reaction (Eq. (3)) [121]. The presence of water should enable the formation of hydrogen via this reaction by thermodynamic reasons. On the other hand the kinetics of the gas phase water-gas shift reaction was known and the reaction rate in supercritical water appeared to be higher than expected from this [121]. The effect of pressure can be considered by calculation: The reactions of small free radicals at increased pressures are faster because of higher collision numbers leading to a better energy nivellation [122]. To consider this, the reaction rate coefficient can be set to the so-called high-pressure limit [123,124]. By doing so, the reaction rate of the measured water-gas shift reaction was still very high. Early studies assumed a lower activation energy by water shell formation around the activated complex [121]. Later this was specified by assuming formic acid as intermediate and a lowering of activation energy for the formation of CO_2 and H_2 by solvation of the activated complex [125,126]. In the second case water as solvent changes selectivities, because the lowering of activation energy is different for the two possible reaction pathways of formic acid in both directions of the water-gas shift reaction. Here formic acid is forced to form CO_2 and H_2 instead of CO and H_2O, because the activated complex formed with water has a lower energy in the first case [125,126].

In supercritical water gasification the water-gas shift reaction is the key reaction as well [87,127]. In this case the kinetic inhibition of this reaction is of importance. The presence of alkali salts is necessary to attain the low CO and high hydrogen yields calculated by thermodynamic studies [30]. The reason is that alkali salts catalyze the water-gas shift reaction [128], as also many heterogeneous catalysts like Nickel [129]. The catalytic effect was connected with the basic character of salts [128] although such argumentation causes problems if the changes in acidity/basicity in near- and supercritical water are considered [130]. So far the reaction pathway and the effect leading to the catalysis are not clear today [130]. In addition the alkali salt concentration in “supercritical” water should be low, because of the decreased solubility. On the other hand, a certain and even low solubility is there and enables the effect of alkali salts. In the gas phase only catalysis on salt particles is possible.

Although it is not fully clear how the alkali salts catalyze the water-gas shift reaction, the result is obvious. Only in the presence of salts the thermodynamic predicted gas composition is reached (below 650 °C, [131]). In addition the hydrogen formed via this reaction is very reactive and influences the reactions occurring. That hydrogen, formed via the water-gas shift reaction, hydrogenates organic compounds was shown be the reaction of deuterated glucose in normal water. Here H_2 was added to double bonds formed via the degradation of glucose, and H_2 could only be formed via the water-gas shift reaction of normal water [111]. This effect was discussed as reason, why a continues stirred tank reactor (CSTR) behaves different concerning gas forming kinetics from a tubular reactor [87,132]. Only in the CSTR hydrogen formed via water-gas shift reaction is able to react with early intermediates. This suppresses polymerization, because these early intermediates are very reactive and react with each other if they are not “saturated” by hydrogen [111].

In the gasification of biomass water is important as reactant for splitting the macromolecules by hydrolysis and as hydrogen source via the water-gas shift reaction. The change of the properties of water by passing its critical point makes the different between liquefaction and gasification in the case no heterogeneous metal catalyst is present. As a solvent the high solubility of intermediates and hydrogen suppresses unwanted solid formation.

6. Perspectives and future directions

The different processes with their various product options from biomass degradation in hot compressed water show the large potential of hydrothermal conversions. Mainly, water opens new reaction pathways compared to "dry processes", needing lower reaction temperatures. This is a consequence of the polar character of water and the high reactivity of biomass with its many polar bonds in water. The change of properties of water enables changes of selectivity – therefore different products can be selected. Compared to dry processes the reached yields of the products are very high. And these are processes for wet types of biomass, which is still a rarely used resource for bioenergy production apart from a few applications such as biogas production by fermentation. The use of residues from agriculture, forestry, and land cultivation as well as from food and feed production will be an increasingly important option in terms of energy supply. The complimentary use of the huge potential of wet and dry types biomass is a challenge. Hydrothermal processes are a promising basis for the production of a variety of different intermediates to be used for energy and chemical purposes.

On the one hand, we know a lot about chemical reactions in sub- and supercritical water. On the other hand, only few technical applications exist. Very important are bench and pilot scale plant to bridge from lab-scale research to industrial application. Examples are the plant of AVA-CO2 for hydrothermal carbonization. It is a multi-batch process; the reactor of the pilot plant has the final size (14 400 L) in view of a production plant, the latter will be six or twelve reactors [133]. Examples for bench-scale plant with a continuous hydrothermal carbonization are from the companies Artec Biotechnologie GmbH [134], SunCoal [135] and terranova [24] also in Germany. The largest plants for gasification with a throughput of 100 kg/h are at the KIT in Germany [49] and 410 kg/h by a coal catalyzed version in cooperation with the University of Hiroshima, Japan. Here, in contrast to other countries also some Japanese companies are strongly involved to develop the technology [136]. Also important are plants in the USA in view of hydrothermal liquefaction processes, e.g. for the so-called STORS (Sludge to Oil Reactor System) process with 30 kg of concentrated sewage sludge (20 wt.% solids) per hour in the Battelle Pacific Northwest laboratories [137]. Even larger, with 200 kg/h the liquefaction of sludge was demonstrated in Japan [138]. Related processes demonstrated in increased scale are the hydrothermal sugar formation by Renmatrix, USA [139] with 3 tons (dry mass) a day. This is of special importance, because it shows that not only "fuels" from biomass are interesting. This seems to be also the impression of the BASF, starting cooperation. Although this summary is likely not complete, it shows the typical sizes of bench and pilot plants and that there are important experiences for scale-up.

On the other hand, there seems to be a "barrier" between research and application. From the view of research, the needs of industry and economy have to be addressed more strongly. This means that whole process chains have to be developed. In the case of biomass this means the chain from the plant on the field to the final product, which might be a fuel or a polymer. This is important, because every process is part of a network, and the other connected production lines have to be integrated, too. In addition, aspects important for scale-up [140] have to be investigated more intensively. For example in SCWG high heating rate are necessary to get the best gas yield. On the other hand, heat exchange is necessary to get reasonable heat efficiency; this is a contradiction. Good heat exchange leads to relative low heating rates. Pumping of concentrated biomass slurries is not possible; therefore mixing with hot process water instead of passing of the biomass through a heat exchanger is suggested. In view of the energy balance, this is no solution [7]. Here more studies to understand the effect and to develop an engineering concept are necessary. In general, more conversions of model compounds than of real biomass are conducted. Model compounds give a better understanding of the chemical process, but studying them completely ignores the effect of the biomass structure on the process. Some exceptions can be found in HTC research [21,96,141].

Also the role and needs of the market have to be considered. As an example, not only the quality of product but also the production costs and available amounts have to be taken into account. Anyway, groups working in the field of hydrothermal conversion research should talk more about "products" than about "processes" to be able to communicate with industry. Such a better communication should be a goal in the future, e.g. by creation of special workshops or platforms e.g. on Internet basis.

To develop process chains instead of single process steps, it would be helpful if there would be more and better funding possibilities between teams in different continents, e.g. Europe and USA. This would initiate new and powerful impacts on research and development.

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